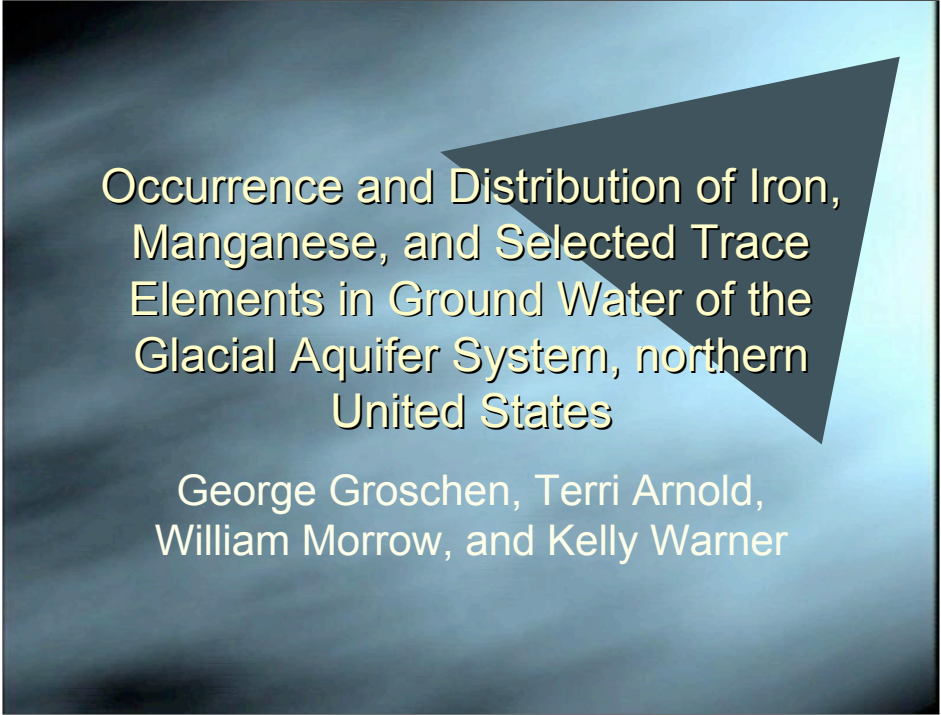




Occurrence and Distribution of Iron, Manganese, and Selected Trace Elements in Ground Water of the Glacial Aquifer System, northern United States

George Groschen, Terri Arnold,
William Morrow, and Kelly Warner

Dissolved trace elements, including iron and manganese, are often an important factor in use of ground water for drinking water supplies in the glacial aquifer system of the northern United States.

Concentrations of dissolved minor and trace elements can vary over several orders of magnitude across local well networks as well as across regions of the US.

Characterization of this variability is a step in determining the regional probability of these trace elements exceeding drinking-water or other human health standards.

Introduction

Glacial aquifer extent

Sb, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn,
Mo, Ni, Se, Sr, Tl, U, V, and Zn.

All NAWQA wells sampled in Glacial
Aquifer

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Page 2.

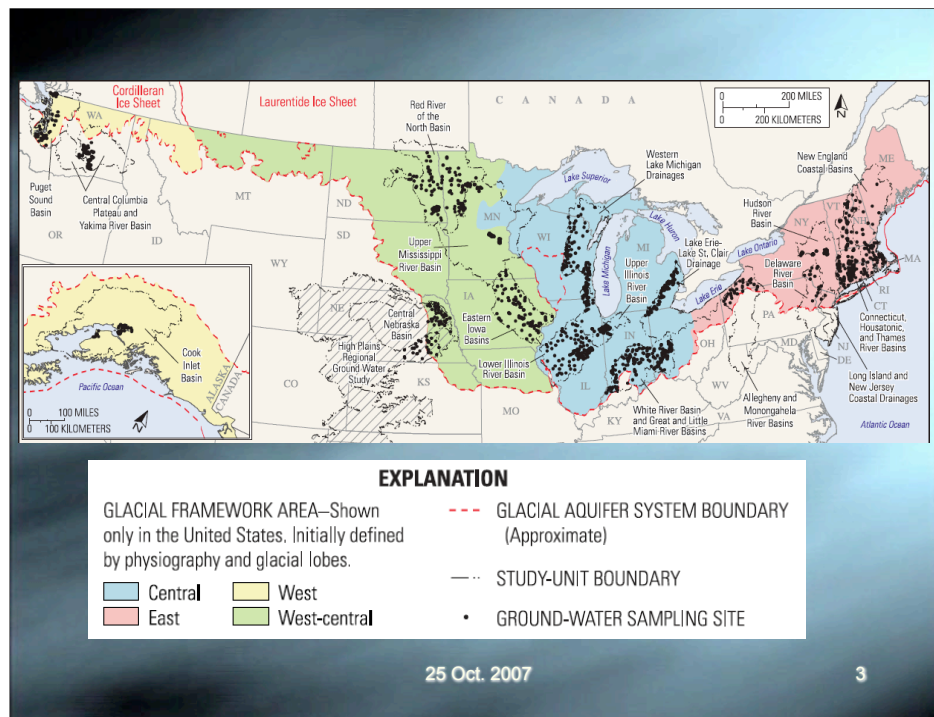
From 1991 through 2003

Trace element concentrations in 847 wells.

Dissolved iron and manganese concentrations were analyzed in those wells and in an additional 743 wells.

The sampled wells are from both land-use monitor well (LUS) networks and water-supply well (MAS née SUS) networks.

Antimony (Sb), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), strontium (Sr), thallium (Tl), uranium (U), vanadium (V), and zinc (Zn).



Page 3.

Glacial Framework areas were developed by Warner and Arnold (2005) to organize the data-collection and interpretation of results for the Glacial principal aquifer.

The map also shows the distribution of wells sampled for iron, manganese, and selected trace elements, NAWQA program.

Methods

Censored data

Summary statistics with Regression on Order Statistics (ROS)

Significant differences by KW, Peto and Peto, maximum likelihood, and Kendall regression (tau)

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Page 4.

Zero (Ba and Sr) to 99 (Ag) percent of analytical results reported as below detection. Those elements with more than 79% data below detection—Sb, Be, Cd, Ag, and Tl—were not examined further except with respect to MCLs.

Regression on Order Statistics (ROS) was used to model probability distributions and estimate medians and other quantiles of the trace element concentrations. Many box plots shown here are based on ROS estimated quantiles.

Kruskal-Wallis for non-censored factors.

For multiply-censored data: Survival statistics...modified for left-censored data

Peto and Peto tests for significant differences between empirical cumulative distribution functions estimated by Kaplan-Meier method.

A few censored regressions using maximum likelihood technique.

Kendall monotonic correlations between continuous variables singly or doubly censored.

Environmental factors

1. Well depth
2. Water use
3. Network type and land use
4. Salinity
5. pH
6. Dissolved oxygen
7. Oxidation-reduction

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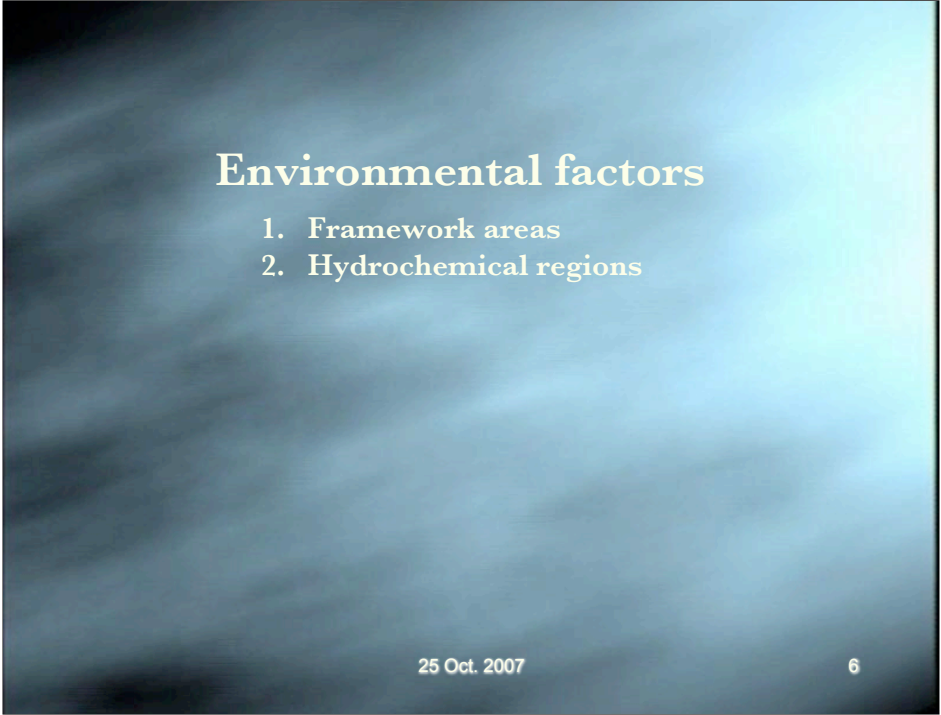
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Page 5.

After basic geographic distribution on a series of maps (not shown in this presentation) we looked at the relationships of the elements to a series of environmental factors.

Well depth, salinity (residue on evaporation at 180° C), pH, DO, and temperature are continuous and used Kendall regression.

Categorical factors, water use, network type/land use, and redox used Peto and Peto test, described later.



Environmental factors

1. Framework areas
2. Hydrochemical regions

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Page 6.

Briefly touch on the significance of Glacial framework areas developed by Warner and Arnold (2005)--surprisingly robust differences among areas with respect to elements.

Short discussion of the relationships among elements and Hydrochemical regions.

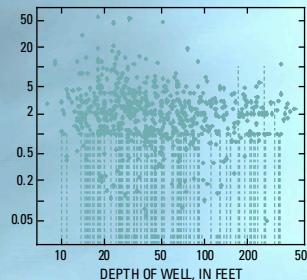
Environmental factors

Well depth

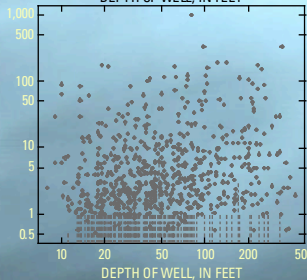
Monotonic Correlation Kendall's τ

Element	Well depth	
	Tau	p-value
Arsenic	0.13	0.0000
Barium	0.04	0.1241
Cobalt	-0.10	0.0000
Chromium	-0.04	0.1225
Copper	0.01	0.8247
Iron	0.09	0.0000
Lithium	0.15	0.0000
Manganese	-0.11	0.0000
Molybdenum	0.01	0.6009
Nickel	-0.12	0.0000
Lead	0.03	0.1916
Selenium	-0.01	0.7548
Strontium	0.07	0.0188
Uranium	-0.04	0.0531
Vanadium	0.03	0.3456
Zinc	0.15	0.0000

Ni



Zn



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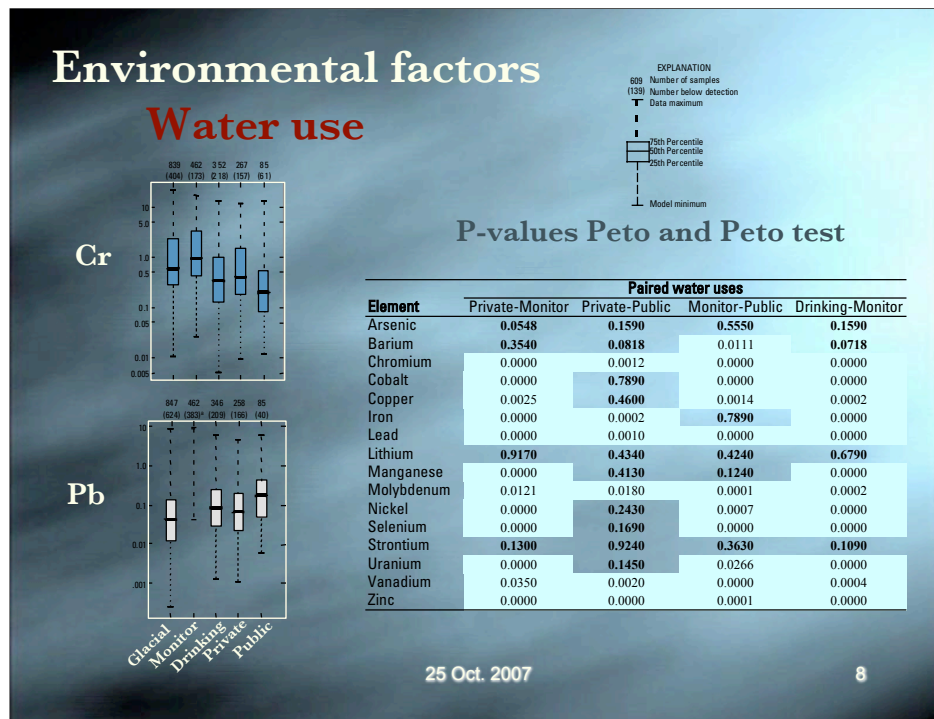
Page 7.

Well depth versus element concentrations:

For Kendall's tau, I've highlighted the correlation coefficients whose absolute value is 0.1 or greater and p-value is less than 0.05 (95% confidence). Tau coefficient ranges from -1 (perfect inverse) to +1 (perfect direct) correlation and is often about 0.2-0.3 lower than a comparable Pearson's R. In yellow cells $p > \alpha$, or the two variables are more or less independent.

As, Li, and Zn are positively (pale green cells) correlated to well depth—concentrations increase as well depth increases. Lithium and zinc are shown in the graphs. Co, Mn, and Ni are inversely correlated (little gray cells). Concentrations are in micrograms per liter.

The procedure "cenxyplot," in "R," plots real data and censored data. The censored values are indicated by dashed lines from the X-axis up to the reporting level for that specific lab result. For Ni there are lot of data values shown below the early 1 $\mu\text{g/L}$ reporting level.



Page 8.

Water use: private-supply, public-supply, drinking-water use (combined public- and private-supply wells) and monitor (unused) wells.

Peto and Peto is modification of G-rho Wilcoxon test. It tests for significant difference between empirical cumulative distribution functions of censored data estimated by Kaplan-Meier method.

Procedure “cendiff” in “R”.

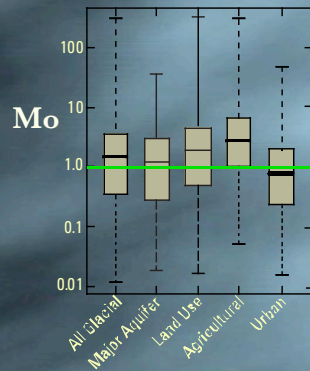
Cr, Pb (shown in box plots), Mo, V, and Zn are significantly different in all comparisons with respect to water use. Lithium and strontium concentration distributions are similar among all water uses.

Box plots (slightly different from “standard”) generally show the range of data to the top and the range of ROS modeled values to the bottom (less than reporting levels) along with IQR and median.

Drinking versus monitor wells show the most differences (right most column).

Environmental Factors

Network Type



P-values Peto and Peto test

Element	Paired network types or land uses.			
	ag urb	ag sus	urb sus	lus sus
Arsenic	0.0000	0.1150	0.0000	0.0309
Barium	0.0975	0.1640	0.0095	0.0192
Chromium	0.5220	0.0000	0.0000	0.0000
Cobalt	0.7950	0.0000	0.0000	0.0000
Copper	0.0019	0.0434	0.0000	0.0002
Iron	0.2130	0.0000	0.0000	0.0000
Lead	0.3610	0.0000	0.0000	0.0000
Lithium	0.0007	0.0175	0.0890	0.4190
Manganese	0.0052	0.9460	0.0115	0.2630
Molybdenum	0.0000	0.0000	0.0180	0.0011
Nickel	0.6820	0.0000	0.0000	0.0000
Selenium	0.0000	0.0000	0.1520	0.0000
Strontium	0.0000	0.0000	0.0760	0.0354
Uranium	0.0000	0.0000	0.4660	0.0000
Vanadium	0.0000	0.0000	0.0003	0.0001
Zinc	0.0723	0.0000	0.0000	0.0000

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Page 9.

Network type—Major aquifer survey wells versus land-use wells

MAS (SUS) wells generally deeper and mostly private- and public-supply wells

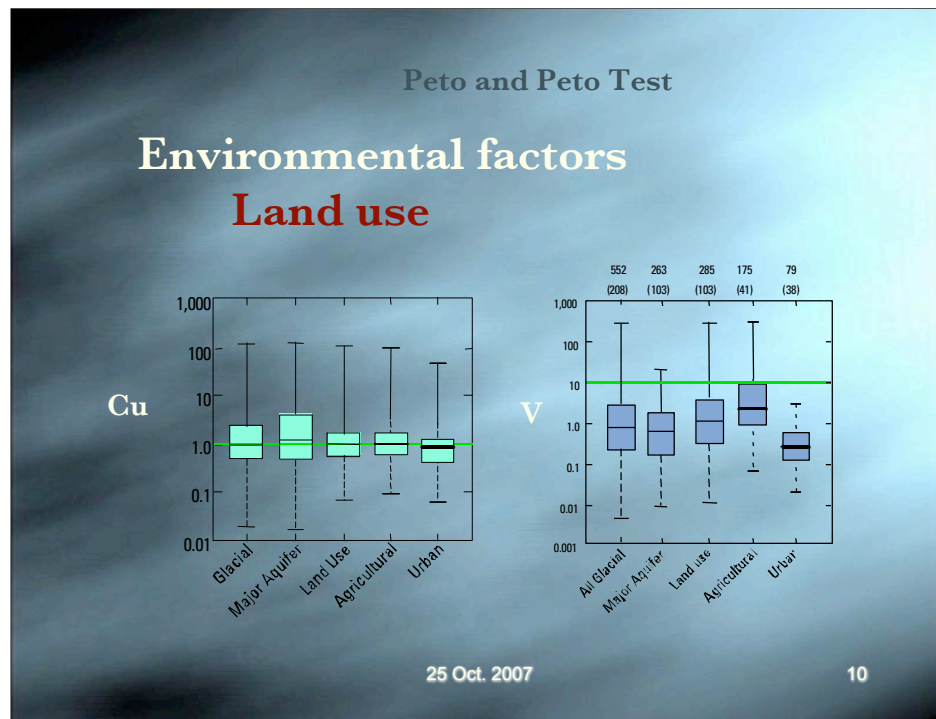
LUS wells shallow—29.6 feet **monitoring** well depth mean

LUS wells are split into agricultural and urban land use.

Cu, Mo, and V are significantly different in all comparisons. Mo on this page and Cu and V on the following page.

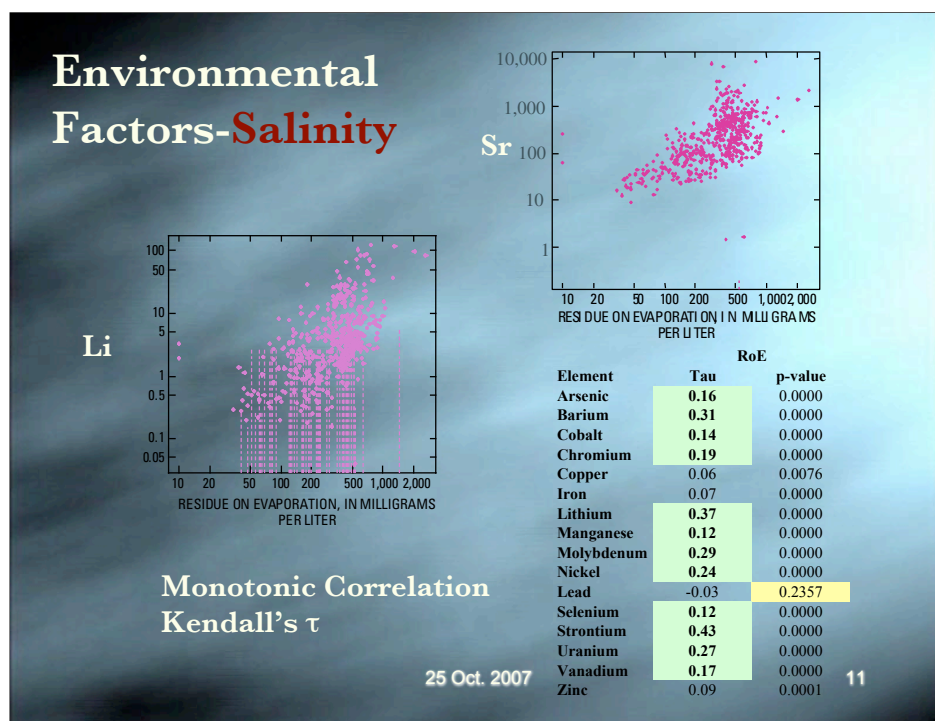
Fewer than half of the elements show no significant difference between agricultural and urban wells 7 of 16 (leftmost column).

LUS wells, as a group, are significantly different from MAS wells for all elements except Li and Mn (rightmost column).



Page 10.

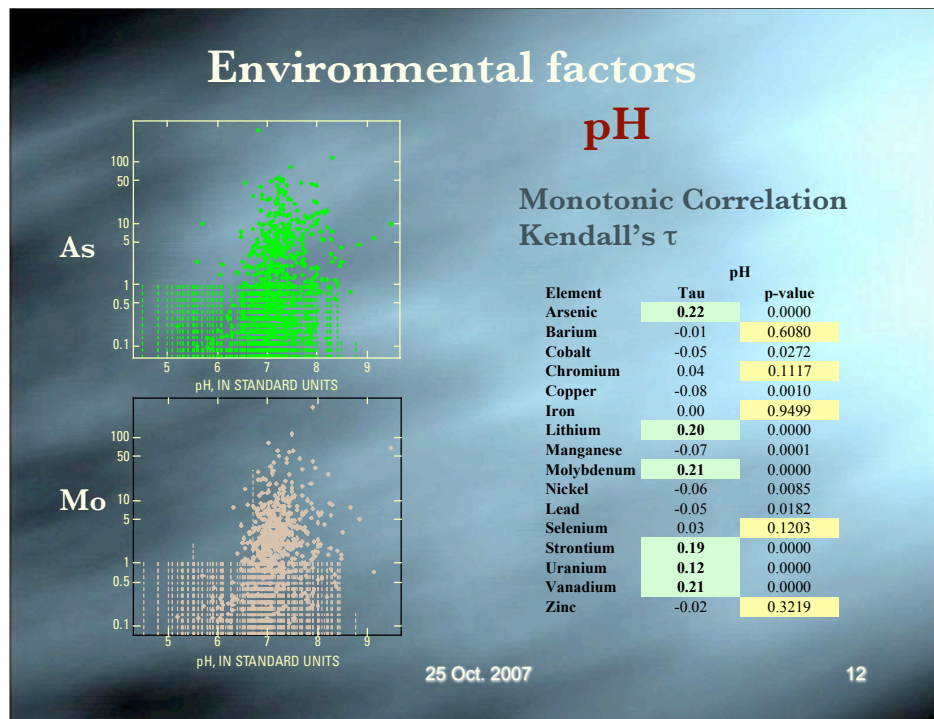
Box plots of lithium and vanadium by land use/network type categories.



Page 11.

Relationships to salinity (residue on evaporation at 180° C)

All elements except Cu, Fe, Pb, and Zn are significantly correlated to salinity. Sr and Li have the largest correlations coefficients and are plotted. Sr has only one censored value and lithium has a substantial number as indicated by the dashed lines from the X-axis to the RL.

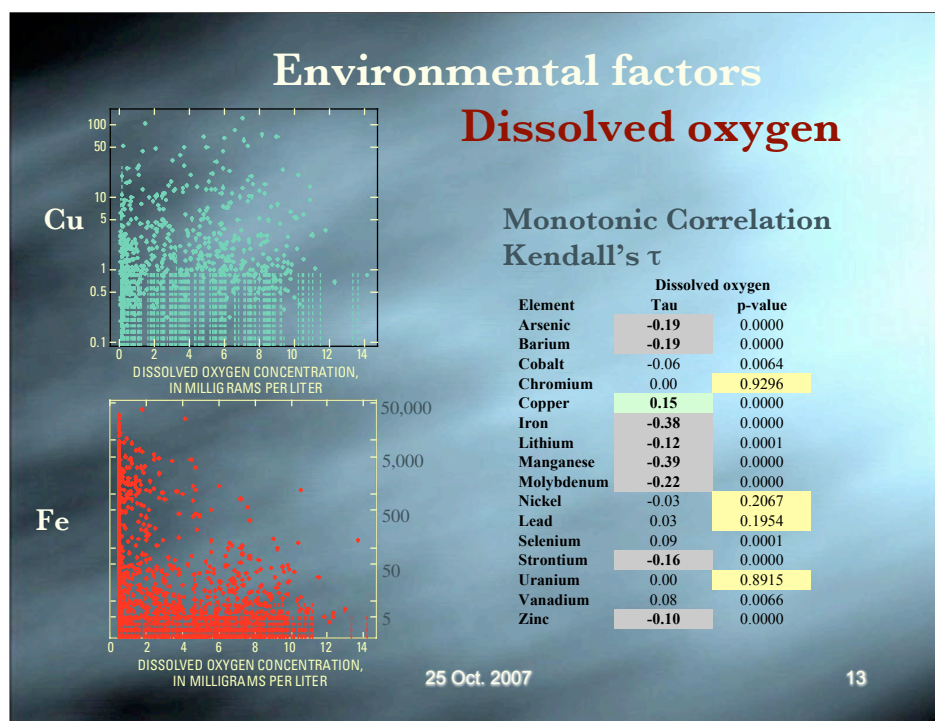


Page 12.

Effects of pH on solubility.

Generally, based strictly on mineral solubility, most of these elements should be more soluble at low pH. The lack of inverse correlations indicates that pH is not an important factor for the Solubilization of these elements.

In fact, As, Li, Mo, Sr, U, and V have direct correlations—as pH increases, these concentrations increase. For some of these, that may indicate a sorption process—some elements more readily desorb from solid phases in the soil or aquifer matrix. That may be the case for As, and Mo.



Page 13.

Dissolved oxygen concentration.

As, Ba, Fe, Li, Mn, Mo, Sr, and Zn are inversely correlated with dissolved oxygen. This is expected for As, Fe, and Mn that are “redox-sensitive” and should be less soluble under oxic conditions.

Co and Cr are also “redox-sensitive” but show no correlation.

Cu is redox sensitive, however, it shows a direct correlation with DO indicating that the oxidized species (II) may be more soluble than the reduced (I).

Ba, Li, and Sr are not “redox sensitive” and should show no correlation, inverse or direct, to dissolved oxygen. Some other process may control these that IS redox sensitive, such as sulfate for Ba.

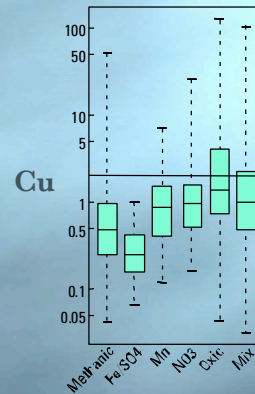
Environmental factors

Oxidation-Reduction

Cu > As > Co = Se > Ba = Cr = Mo > Ni = U > Sr = Pb > Li = V > Zn

Peto and Peto test p values

Barium	Fe/SO4	Mn	NO3	Oxic	Mix
Methanic	0.0000	0.0000	0.0001	0.0000	0.0000
Fe/SO4		0.1060	0.0952	0.0000	0.6900
Mn			0.9040	0.2790	0.1200
NO3				0.2890	0.0895
Oxic					0.0000
Cobalt	Fe/SO4	Mn	NO3	Oxic	Mix
Methanic	0.2570	0.1330	0.4800	0.0780	0.0051
Fe/SO4		0.2720	0.0234	0.0000	0.0043
Mn			0.0081	0.0000	0.4270
NO3				0.4810	0.0005
Oxic					0.0000
Copper	Fe/SO4	Mn	NO3	Oxic	Mix
Methanic	0.0023	0.0000	0.0000	0.0000	0.0000
Fe/SO4		0.0079	0.0008	0.0000	0.0000
Mn			0.7490	0.0100	0.3920
NO3				0.0390	0.7880
Oxic					0.0002



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Page 14.

Order of the significance of the redox categories based on significance of binary comparisons (Peto and Peto). The number of blue-shaded cells where $p < 0.05$.

As indicated on the previous page, copper shows increases (box plot) in concentration as the redox category becomes more oxic (from left to right: methanic to oxic).

There is substantial DO in 80% of the “mix” samples (rightmost box). The Mn, NO3, and Mix categories are roughly similar with respect to Cu.

Environmental factors

Framework areas

Peto and Peto test p values

Element	Paired Glacial Framework areas					
	East-Central	East-West Cen	East-West	Central-West Cen	Central-West	West Cen-West
Arsenic	0.0000	0.0000	0.0000	0.0000	0.0000	0.2170
Barium	0.0000	0.0000	0.5220	0.0001	0.0000	0.0000
Chromium	0.0000	0.0000	0.0494	0.0000	0.0218	0.0000
Cobalt	0.0000	0.0000	0.0044	0.0229	0.0197	0.0001
Copper	0.2170	0.0107	0.2920	0.0000	0.0031	0.2650
Iron	0.0004	0.0001	0.0000	0.3320	0.0000	0.0000
Lead	0.0000	0.0005	0.0180	0.0003	0.0000	0.1680
Lithium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Manganese	0.8580	0.0009	0.0000	0.0000	0.0000	0.0000
Molybdenum	0.0000	0.0000	0.0000	0.0465	0.0619	0.0020
Nickel	0.0003	0.0000	0.0154	0.0000	0.0000	0.0000
Selenium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Strontium	0.0000	0.0000	0.0000	0.0000	0.0000	0.9360
Uranium	0.0000	0.0000	0.0000	0.0000	0.0000	0.1350
Vanadium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Zinc	0.0000	0.2060	0.1860	0.0000	0.6980	0.0000

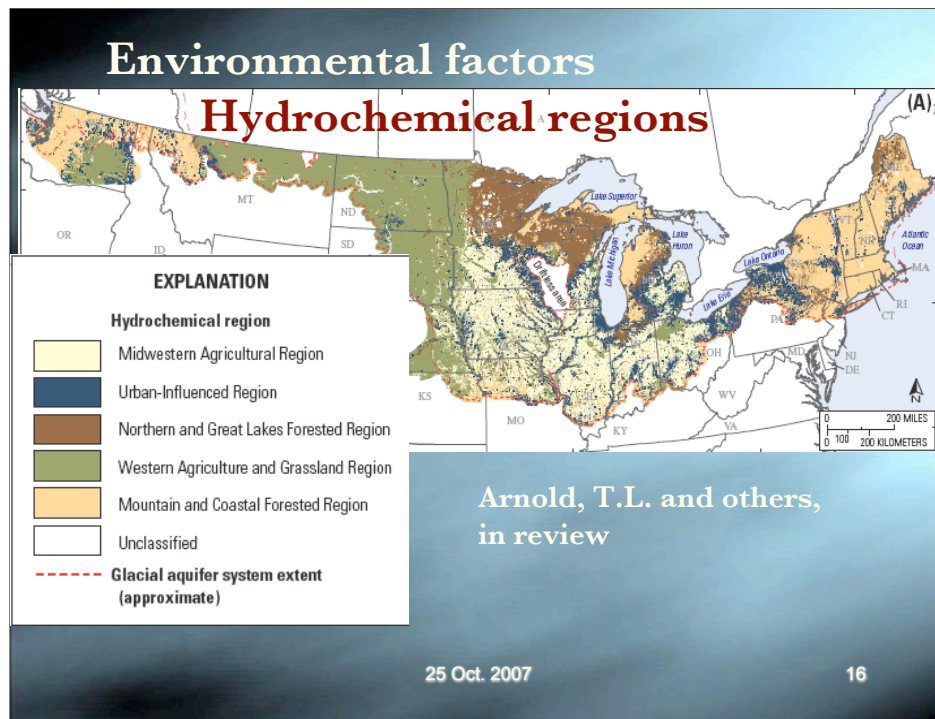
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Page 15.

Relation to Glacial Framework areas.

Except for Zn, all elements are significantly different from area to area with a few exceptions. It is surprising that there are so many significant differences because the areas are based on a primarily empirical stratification scheme.



Page 16.

A map of the hydrochemical regions developed by Arnold and others (in review).

Hydrochemical Regions P-values Peto and Peto test

Arsenic	NGLFR	WAGR	UIR	MCFR
MAR	0.0116	0.0048	0.0000	0.0000
NGLFR		0.5930	0.0000	0.0000
WAGR			0.0000	0.0000
UIR				0.0000

Cobalt	NGLFR	WAGR	UIR	MCFR
MAR	0.4090	0.0000	0.0000	0.0000
NGLFR		0.0000	0.0130	0.0000
WAGR			0.0000	0.4930
UIR				0.0000

Lithium	NGLFR	WAGR	UIR	MCFR
MAR	0.0060	0.0000	0.0000	0.0000
NGLFR		0.0000	0.0000	0.0000
WAGR			0.0000	0.3290
UIR				0.0000

Uranium	NGLFR	WAGR	UIR	MCFR
MAR	0.0237	0.0000	0.0000	0.0000
NGLFR		0.0003	0.0000	0.0000
WAGR			0.0000	0.0018
UIR				0.0000

Copper	NGLFR	WAGR	UIR	MCFR
MAR	0.2650	0.0876	0.0002	0.2530
NGLFR		0.0180	0.0170	0.7770
WAGR			0.0000	0.0345
UIR				0.0844

Manganese	NGLFR	WAGR	UIR	MCFR
MAR	0.3680	0.0807	0.0767	0.0000
NGLFR		0.4930	0.2120	0.0097
WAGR			0.3770	0.0552
UIR				0.6810

Lead	NGLFR	WAGR	UIR	MCFR
MAR	0.1650	0.4330	0.0000	0.0000
NGLFR		0.9390	0.0148	0.0018
WAGR			0.0005	0.0002
UIR				0.0330

Zinc	NGLFR	WAGR	UIR	MCFR
MAR	0.4710	0.0143	0.7600	0.0022
NGLFR		0.0086	0.8410	0.0018
WAGR			0.0218	0.8430
UIR				0.0090

Midwestern Agricultural (MAR)
Northern and Great Lakes Forested (NGLFR)
Western Agricultural and Grassland (WAGR)
Urban-influenced (UIR)
Mountain and Coastal Forested (MCFR)

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Selected test results for hydrochemical regions.

Left side are those with the largest number of significant differences in binary comparisons.

Right side, fewest.

Drinking-water implications

MCLs

- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Selenium
- Thallium
- Uranium

Lifetime Health Advisory

- Manganese
- Molybdenum
- Nickel
- Silver
- Strontium
- Zinc

Action levels

Copper and Lead rule

These are human-health benchmarks

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Three general steps were followed for evaluating ground-water-quality data in a human-health context.

Concentrations were compared with USEPA assigned MCL or AL or a Health-based screening level (HBSL) developed by Toccalino and Norman, 2006).

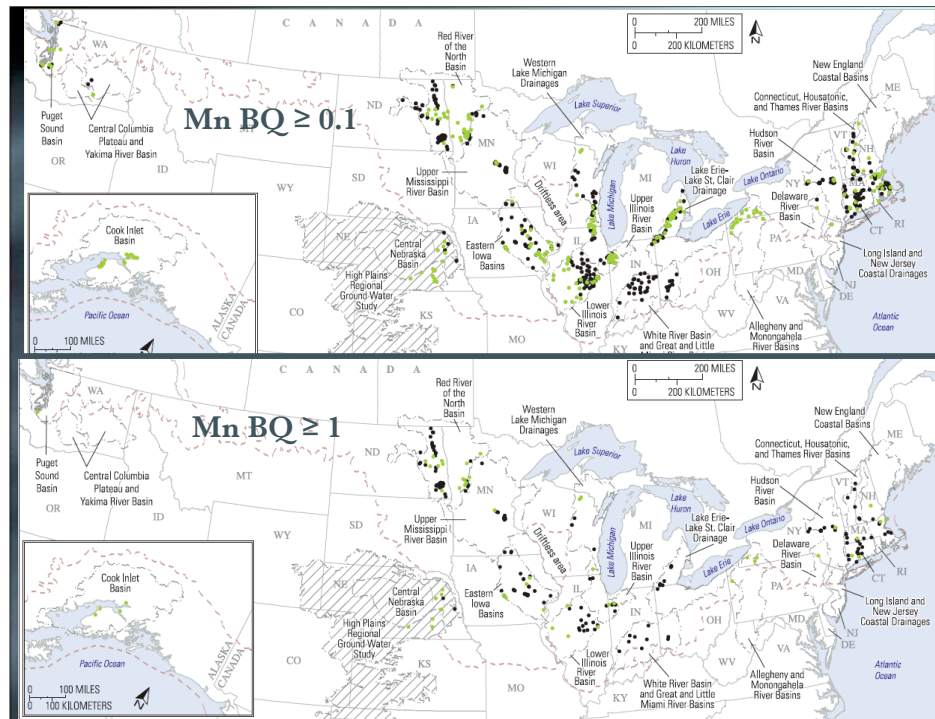
Human health concern was identified by calculating Benchmark Quotients (BQs) for individual elements.

BQs are ratios of the sample concentration to their respective MCL, AL, or HBSL.

A quotient near 1 indicates that the concentration in the sample is close to the MCL, AL, or HBSL. A quotient greater than one indicates the sample concentration is greater than the associated MCL, AL, or HBSL.

Level of concern is when $BQ \geq 0.1$.

Toccalino, P.L., and Norman, J.E., 2006, Health-Based Screening Levels to Evaluate U.S. Geological Survey Ground water Quality Data: Risk Analysis, Vol. 26, No. 5, pp. 1339–1348.



Page 19.

Maps of Manganese benchmark quotients in the glacial aquifer system.

827 samples (52 percent) had a BQ ≥ 0.1 (top map)

305 samples (19 percent) had BQ ≥ 1 (bottom map).

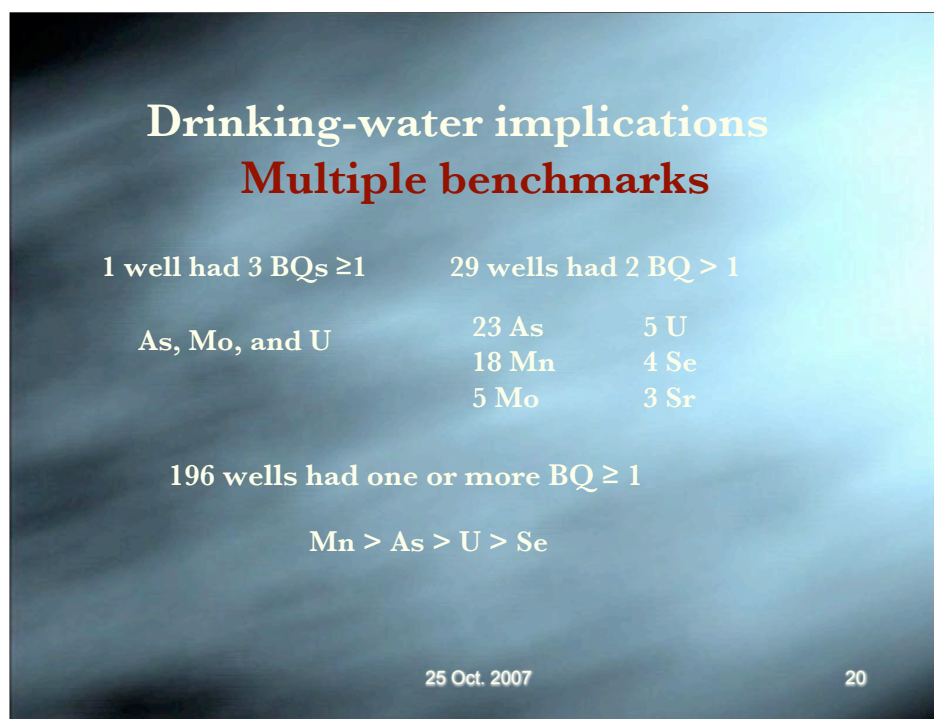
By glacial framework area, the 304 wells that had a manganese BQ greater than or equal to 1 were distributed as follows:

58 of 329 (18 percent) were East area wells;

83 of 651 (13 percent) were Central wells;

158 of 443 (36 percent) were West-central wells; and

5 of 167 (3 percent) were West wells.



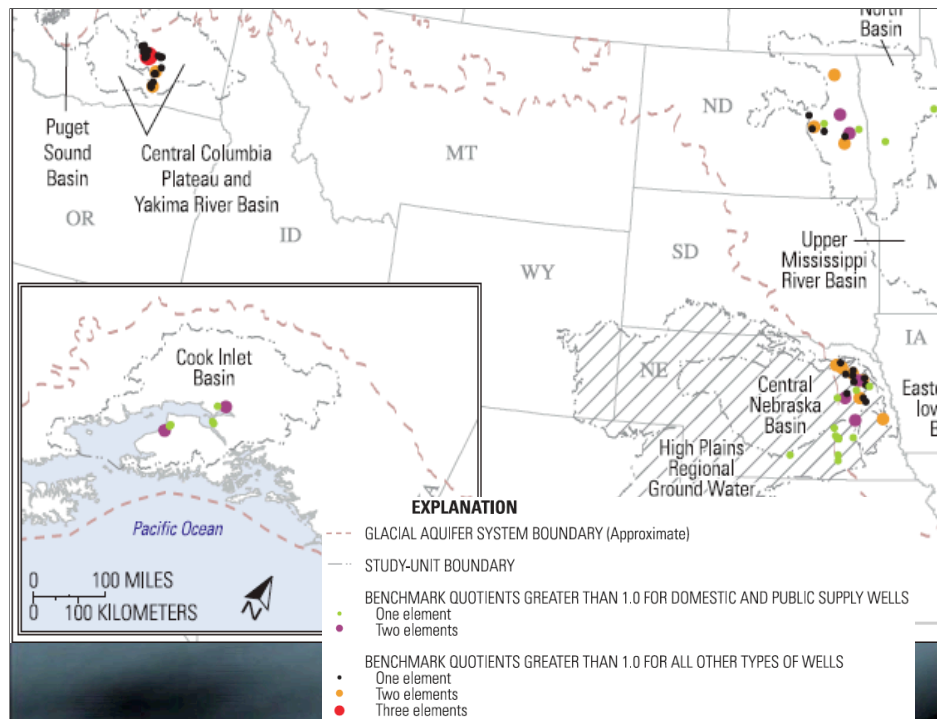
Page 20.

Manganese most often exceeded its benchmark (LHA) in the glacial aquifer system wells. Of the 1,590 wells sampled for manganese, only 556 are private or public drinking-water supplies and of those, 9.9 percent (55) exceeded the manganese LHA.

Fewer wells had concentrations of arsenic, selenium, or uranium that exceeded relevant health-based benchmarks in part because only about 847 samples were analyzed for most trace elements.

Most concentrations that exceeded a relevant health-based benchmark were from West-central area (Iowa, Minnesota, North and South Dakota, Nebraska, and Kansas) wells, however, there is little geographical pattern to the wells with concentrations of concern.

The full implications to human health can not be assessed without information on the population served by the wells that had concentrations of concern.

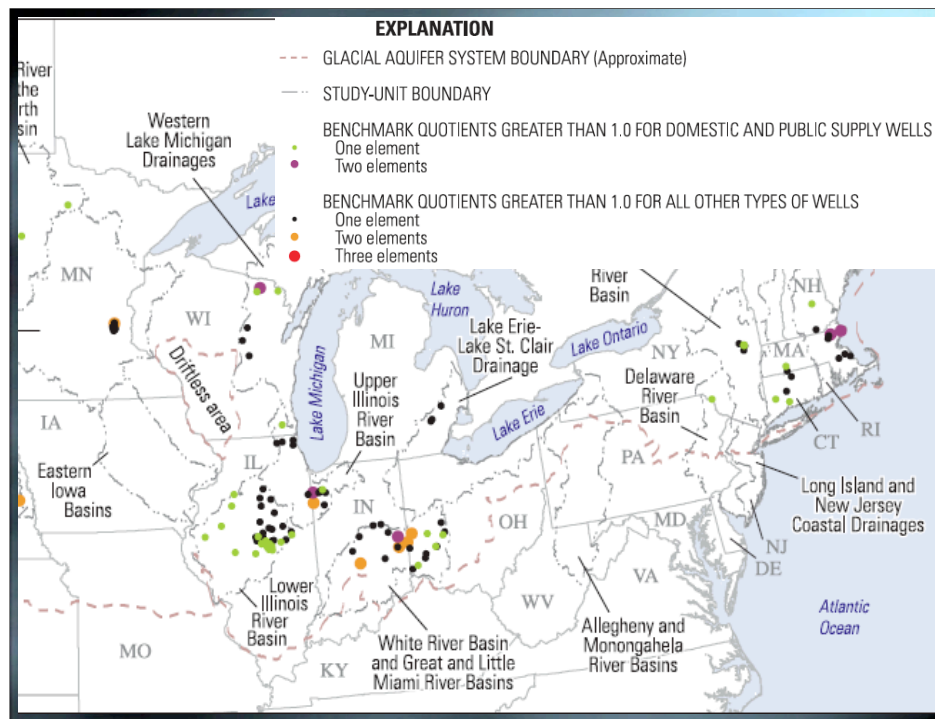


Page 21.

Split the map into east and west (West above) to better examine the location of wells with multiple elements with $BQ \geq 1.0$.

Mucus green for drinking-water wells (private- or public-supply) with a single element and purple for two elements.

Non-drinking wells (mostly monitor wells) Black-one, orange-two, and red-three. Only one well (ag-land use, monitor) had 3 $BQs \geq 1$. It is in Washington (CCYK).



Page 22.

Split map into east and west (East above) to better see the location of wells with multiple elements with $BQ \geq 1.0$.

Mucus green for drinking-water wells (private- or public-supply) with a single element and purple for two elements.

Non-drinking wells (mostly monitor wells) Black- one, orange-two and red-three. No wells in the eastern half had 3 $BQs \geq 1$. However,

CONCLUSIONS

1. Well depth
2. Water use
3. Network type–land use
4. pH
5. Salinity
6. Oxidation-reduction
7. Framework areas
8. Hydrochemical regions
9. Drinking-water implications

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Concluding remarks

Looked at the relationships among environmental variables and element concentration distributions in the Glacial aquifer system.

For the elements that were above benchmarks or at a level of concern (1/10 of a benchmark):

Well depth was important for As, Mn, Ni, and Zn

Water use was important for Mo, U, Se, Ni, Pb, and Zn

Network-type/land use was important for As, Mo, U, Sr, Se, Ni, Pb, and Zn.

pH was generally unimportant except for As, Mo, U, and Sr

Salinity was important for all but Pb and Zn.

Redox was important for As and Se.

Glacial Framework areas are useful for all these elements

Hydrochemical regions are useful for all except Mn.

Elements with BQs ≥ 0.1

ELEMENT	NUMBER OF SAMPLE S	WELLS SAMPLE D	PERCENT T OF WELLS	WELL DEPTH	pH	SALINITY	DISSOLVED OXYGEN
Manganese	827	1590	52%	I	N	D	I
Arsenic	339	833	41%	D	D	D	I
Molybdenum	198	847	23%	N	D	D	I
Uranium	162	832	19%	N	D	D	N
Strontium	157	552	28%	N	D	D	I
Barium	118	847	14%	N	N	D	I
Selenium	46	833	5.5%	N	N	D	N
Nickel	33	847	3.9%	I	N	D	N
Lead	19	847	2.2%	N	N	N	N
Thallium	4	480	0.8%	U	U	U	U
Zinc	4	847	0.5%	D	N	N	I

	FAREA	HCR	WATER USE	NETWORK- LAND USE	REDOX
Manganese	5	2	2	2	0
Arsenic	5	9	0	3	10
Molybdenum	5	9	4	4	7
Uranium	5	10	3	3	6
Strontium	5	8	0	3	5
Barium	5	7	1	2	7
Selenium	6	9	3	3	8
Nickel	6	6	3	3	6
Lead	5	7	4	3	5
Thallium	0	0	0	0	0
Zinc	3	6	4	3	3
Cadmium	0	0	0	0	0
Beryllium	0	0	0	0	0

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Page 24.

Does anybody really know what time it is?

Does anybody really care?

About time.

If so I can't imagine why...oh no.

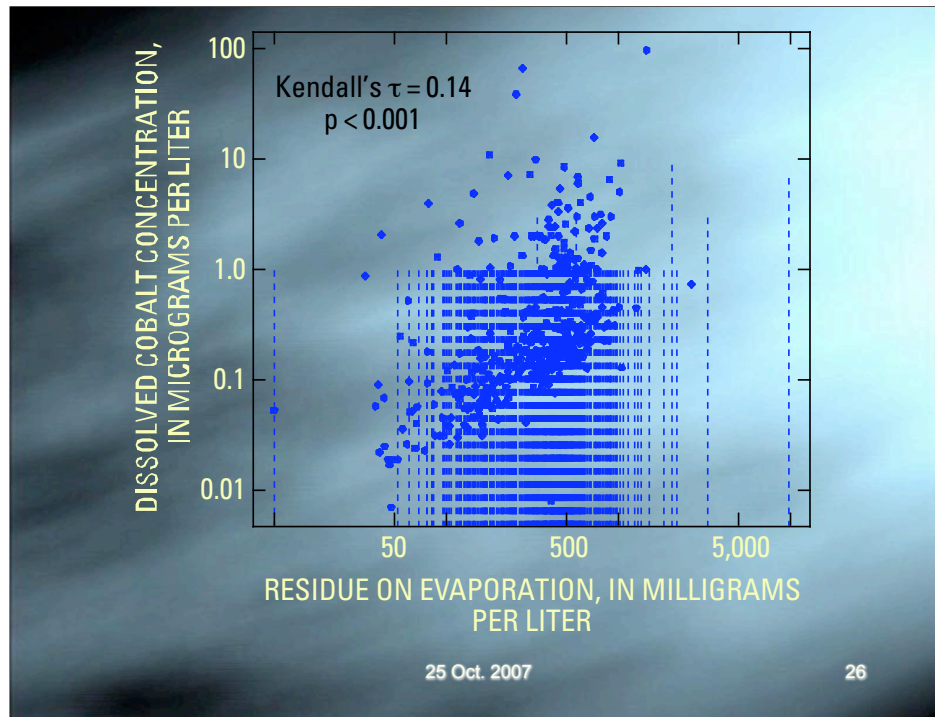
We've all got time enough to cry.

Chicago Transit Authority



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This is the end.



Page 26.

A large example of a censored X-Y plot if a relevant question is asked